Electrochemical Reduction of Pyridine- and Benzene-Substituted *n*-Alkyl Esters and Thioic *S*-Esters in Acetonitrile

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Bulk controlled potential electrolysis experiments have been performed on a wide range of *n*-alkyl-substituted esters and thioic *S*-esters of pyridine and benzene in dry acetonitrile with tetraalkylammonium salts as the supporting electrolyte. In most cases, the bulk one-electron reduction of oxygen esters results in unstable or semistable radicals being formed that decompose via loss of the alkyl radical to leave the carboxylate anion in high yield (*ca.* 70−100%). Benzoate and dinicotinate esters are the exception to this where the final decomposition products are numerous and complicated. For the thioic *S*-esters, two types of decomposition mechanism have been identified as operating depending on the stability of their anion radicals. Thioic *S*-ester radical anions that are very unstable (lifetimes in the order of several milliseconds) decompose with loss of the thiolate ion to leave a neutral acyl radical that undergoes aromatic substitution reactions with other acyl radicals to form, among other products, γ-lactones. Thioic *S*-esters radical anions that are stable for many minutes to hours ultimately decompose via reaction with molecular oxygen to form carboxylate anions.

Introduction

Recently, we reported the voltammetric behavior of all the mono- and disubstituted alkyl (alkyl = Pr and some Et and Me) pyridine and benzene esters [ArC(O)OR] and several of their thioic *S*-ester [ArC(O)SR] analogues, and the EPR spectroscopy of many of their associated anion radicals[1] (for brevity and clarity the thioic *S*-esters will be referred to as (S) esters and the oxygen esters as (O) esters). The compounds can all be reduced by one electron at negative potentials [−1.61 to −2.69 V *vs* Fc/Fc^+ (Fc = ferrocene)] with several of the compounds also exhibiting a second reduction step. Surprisingly, the stability of the anion radicals formed during the first (least negative) reduction step and the electrochemical reversibility of the reduction process, as measured by cyclic and linear sweep voltammetry, varied considerably between the compounds. Using cyclic voltammetry, many of the compounds were shown to display chemically reversible electrochemical behavior at slow scan rates ($v \leq 100$ mV s^{-1}), indicating that the anion radicals formed were stable for at least several seconds, and their existence was confirmed by EPR spectroscopy. In contrast, other compounds clearly showed chemically irreversible behavior at slow scan rates, indicating that the associated anion radicals of these compounds were much less stable and quickly decompose to form other products. (The terms chemical reversibility or chemical irreversibility when used in conjunction with cyclic voltammetry refer to the stability of the reduced form of the molecules and do not imply thermodynamic reversibility or irreversibility with respect to the electron-transfer step).

Nearly all the other electrochemical studies performed on benzene-based esters in aprotic media have been performed on the reduction of benzoate esters. Wagenknecht *et al.*[2] reported that in acetonitrile, reduction of benzoate alkyl esters leads to relatively stable radical anions that decompose via cleavage of the oxygen alkyl bond to form the carboxylate anion and the alkyl radical, at least at low concentrations (1 mM). At higher concentrations or longer time scales the final products isolated were found to be often much more complicated. Wagenknecht *et al.* also reported that the rate of cleavage of the free radical is related to the stability of the cleaved radical group. For example, the methyl and ethyl ester were found to be more stable than the *tert*-butyl ester. Gul'tyai *et al.*[3] reported that cleavage of the oxygen alkyl bond was the primary decomposition pathway of the reduction of methyl benzoate in DMF and obtained the benzoate anion in 100% yield. In contrast, other workers[4] have reported forming benzoylacetonitrile in high yield from the reduction of methyl benzoate in acetonitrile (i.e., cleavage of the C(O)−O bond). In the bulk reduction of phenyl benzoate[5,6] in acetonitrile it was found that cleavage of the carbonyl carbon oxygen bond occurs, in this case to form phenate and the dianion of benzil. The studies on benzoate esters outlined above show that there exists some ambiguity as to whether the final decomposition products arise from oxygen alkyl bond cleavage or from carbonyl oxygen bond cleavage and whether there is a difference between alkyl and aryl esters.

There have also been several studies dealing with the electrochemistry of sulfur esters. Falsig and Lund[7] reported in the analogous compound to the benzoate ester

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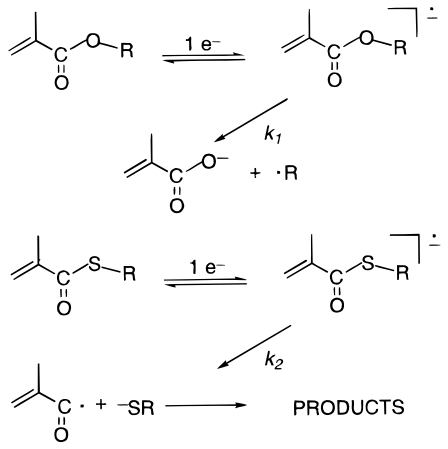
Scheme 1



described above that when the oxygen in the ester is replaced with a sulfur the thioic *S*-esters are reduced to form diphenylacetylene, the benzoic acid anion, and the thiolate. Although the mechanism for the reduction is complicated, it would appear that the principal products resulted from cleavage of the carbonyl sulfur bond rather than the sulfur alkyl bond. An $S_{RN}1$ reaction has been reported where *S*,*S*-diphenyl benzene-1,2-dicarbothioate is reductively reduced to form the isomeric 3,3-bis(phenylthio)pththalide.[8] Electrochemically induced cleavage of the thiocarbonyl sulfur bond in dithioates [−C(S)S−] also has been reported[7,9] for reactions performed in aprotic solvents. However, often the final products of these reactions are numerous and the reaction mechanisms very complicated.

Work from these laboratories[10] has recently demonstrated that the electrochemical reduction of dipropyl pyridine-2,6-dicarboxylate results in the stepwise cleavage of the propyl groups as alkyl radicals to leave the carboxylate anions in close to 100% yield (Scheme 1). In contrast, reduction of the thioic *S*-ester analogue results in the cleavage of the carbonyl sulfur bond to most likely form the neutral carbonyl aromatic radical (acyl radical) that subsequently undergoes a series of additional reactions.

In this paper, we build on the knowledge gained from our earlier studies and work of others to determine the principal mode of decomposition of aromatic (O) and (S) ester radical anions. The possible role that electrochemical reversibility, redox potential, and stability of the anion radicals have in determining the final reaction products is also discussed.

Results and Discussion

The cells used for controlled potential electrolysis experiments have been described previously[10] and consisted of a large volume (100 mL) cell for electrolyzing gram quantities of material and a small volume (5 mL) cell for electrolyzing milligram quantities. Preparative-scale controlled potential electrolysis (CPE) at a GC electrode was performed initially on *ca*. 100 mg samples in the small volume cell. Where it was apparent (by NMR spectroscopy and TLC) that the products of the reduction reactions were complicated, the reductions were also performed in the large volume cell in order to generate more product. All solutions were thoroughly deoxygenated with high-purity nitrogen or argon prior to and during analysis. The potential for the electrolysis was set at the $E_{1/2}$ value as determined by differential pulse voltammetry ($E_{1/2}$ values are given in ref 1). This resulted in slightly lower currents and longer electrolysis times than would maximally be possible when potentials are set at more negative values but ensured that secondary species were not further reduced. Other details regarding the experimental procedures are given in the Experimental Section.

Table 1. Controlled Potential Coulometry (CPC) Data Obtained in a 5 mL Cell for the Number of Electrons Transferred (*n*) for Process 1, Obtained at 20 ± 1 °C in MeCN with Et_4NPF_6 as the Supporting Electrolyte[a]

compd	low concn (5−10 mM) *n*	high concn (70−100 mM) *n*
pyridine esters		
propyl pyridine-3-carboxylate	1.03 ± 0.05	1.03 ± 0.10
propyl pyridine-2-carboxylate	1.05 ± 0.05	0.91 ± 0.10
propyl pyridine-4-carboxylate	0.97 ± 0.05	0.89 ± 0.10
dipropyl pyridine-2,3-dicarboxylate	1.01 ± 0.05	1.08 ± 0.05
dipropyl pyridine-2,6-dicarboxylate[b]	1.01 ± 0.05	0.94 ± 0.05
diethyl pyridine-2,6-dicarboxylate[b]	1.03 ± 0.05	ND
dimethyl pyridine-2,6-dicarboxylate[b]	1.04 ± 0.05	ND
dipropyl pyridine-3,5-dicarboxylate	1.44 ± 0.10	0.87 ± 0.10
dipropyl pyridine-3,4-dicarboxylate	0.94 ± 0.10	0.97 ± 0.10
dipropyl pyridine-2,4-dicarboxylate	1.07 ± 0.05	1.23 ± 0.15
dipropyl pyridine-2,5-dicarboxylate	1.03 ± 0.05	1.05 ± 0.10
diethyl pyridine-2,5-dicarboxylate	1.05 ± 0.10	ND
dimethyl pyridine-2,5-dicarboxylate	1.07 ± 0.05	ND
benzene esters		
propyl benzenecarboxylate	1.50 ± 0.20	1.47 ± 0.20
dipropyl benzene-1,3-dicarboxylate	1.23 ± 0.10	1.14 ± 0.15
dimethyl benzene-1,3-dicarboxylate	1.18 ± 0.10	1.10 ± 0.10
dipropyl benzene-1,2-dicarboxylate	1.20 ± 0.20	1.09 ± 0.10
dipropyl benzene-1,4-dicarboxylate	1.10 ± 0.10	1.08 ± 0.10
dimethyl benzene-1,4-dicarboxylate	1.10 ± 0.05	ND
hexamethyl benzenehexacarboxylate	1.07 ± 0.05	ND
pyridine thioic *S*- esters		
S,*S*-dipropyl pyridine-2,5-dicarbothioate	1.05 ± 0.10	1.03 ± 0.10
S,*S*-dipropyl pyridine-2,6-dicarbothioate	1.10 ± 0.10	1.21 ± 0.20
benzene thioic *S*-esters		
S,*S*-dipropyl benzene-1,3-dicarbothioate	1.05 ± 0.10	1.15 ± 0.20
S,*S*-dipropyl benzene-1,4-dicarbothioate	1.03 ± 0.10	1.03 ± 0.10

[a] Calculated from the equation $N = Q/nF$. Data represent the average of several experiments at concentrations between 5−10 mM and 70−100 mM. ND = not determined. [b] Data from ref 10.

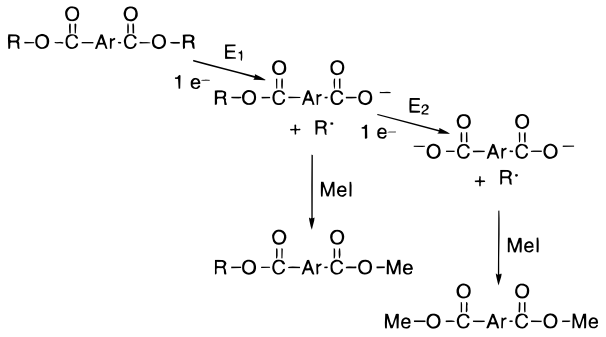
1. (O) Esters. Controlled potential coulometry (CPC) experiments were conducted in the small volume (5 mL) cell under low concentration (<10 mM) and high concentration (>0.7−0.1 M) conditions in acetonitrile (0.1−0.2 M Et_4NBF_4). In order to minimize the effects of impurities and capacitance current on the overall calculated charge, the experiments were performed at an analyte concentration of at least 5 mM. At this concentration it was found that the contribution of the background current was negligible. The data for the number of electrons transferred for the first (least negative) process and calculated from

$$N = Q/nF \quad (1)$$

are given in Table 1[N = no. of moles, Q = charge (coulombs), n = no. of electrons, and F = Faraday's

(8) Praefcke, C.; Weichsel, C.; Falsig, M.; Lund, H. *Acta Chem. Scand., Ser. B* **1980**, *34*, 403.
(9) Voss, J.; Von Bülow, C.; Drews, T.; Mischke, P. *Acta Chem. Scand., Ser. B* **1983**, *37*, 519.
(10) Webster, R. D.; Bond, A. M.; Schmidt, T. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1365.

Scheme 2[a]



[a] E_1 and E_2 = applied potential 1 and potential 2, respectively. R = alkyl. MeI = methyl iodide.

constant]. The data for each compound represent the average of several experiments, and therefore, the exact concentration in each case is not listed. Instead, the average value obtained at a low concentration (5−10 mM) and at a high concentration (70−100 mM) is given, which illustrates that for the (O) esters the number of electrons transferred in the first process is essentially the same at high and low concentrations. The experiments were conducted on Pr esters, primarily because it was thought that the hydrophobic propyl groups would facilitate the extraction of the products from the electrolyte at the completion of the bulk reductions. We found previously that there was very little difference in the electrochemical behavior of Me, Et, and Pr esters in terms of the stability of the anion radicals formed by reduction and the potential of reduction (the Me esters are easier to reduce than the Et and Pr esters by 10−20 mV).[1,10]

For most of the compounds the data from Table 1 indicate that on the long voltammetric time scale one electron is transferred per molecule, which is in agreement with the data obtained using shorter time scale CV and hydrodynamic voltammetric techniques.[1,10] Voltammetric monitoring of the electrolysis experiments showed no anion radicals to be present shortly after the completion of the electrolysis, indicating that the process is not chemically reversible on the synthetic time scale. The simplest explanation for this observation is that the compounds undergo a simple EC mechanism [reversible (or near reversible) electron transfer−chemical reaction sequence] on long time domains and that any intermediate products do not undergo further reduction. The only exceptions to this are propyl benzoate and dipropyl pyridine-3,5-dicarboxylate. The calculated number of electrons transferred for the benzoate ester at high and low concentrations is between one and two, which suggests intermediate species are also being reduced on the long time scale. For the dinicotinate ester more electrons are transferred per molecule at low concentration than at higher concentrations, which indicates that even more complicated electrochemical behavior is occurring (see further discussion below).

It was found that all of the compounds, with the exception of propyl benzoate and dipropyl pyridine-3,5-dicarboxylate (which will be discussed separately), reacted in the same manner, as illustrated in Scheme 2.

The one-electron bulk reduction of the carboxylates ultimately produced the carboxylate anions (73−95%) via cleavage of the oxygen alkyl bonds. The counterion for the carboxylate anions is the supporting electrolyte cation, Et_4N^+. This is essentially the identical reaction we reported previously for the electrochemical reduction

Table 2. Yields of Products Obtained (after Methylation) from the Bulk Electrochemical Reduction of (O) Esters by 1 ± 0.2 Electrons per Molecule at High Concentration (0.07−0.1 M) in MeCN (0.1−0.2 M Et_4NBF_4 or Et_4NPF_6)[a]

starting compd	% yield of methyl ester [ArC(O)OMe] or [RO(O)CArC(O)OMe]
pyridine esters	
propyl pyridine-2-carboxylate	93
propyl pyridine-3-carboxylate	77
propyl pyridine-4-carboxylate	92
dipropyl pyridine-2,3-dicarboxylate	90 (1:5)
dipropyl pyridine-2,4-dicarboxylate	85 (1:0)
dipropyl pyridine-2,5-dicarboxylate	93 (1:1)
dipropyl pyridine-2,6-dicarboxylate[b]	95
dipropyl pyridine-3,4-dicarboxylate	88 (ND)
benzene esters	
dipropyl benzene-1,2-dicarboxylate	74
dipropyl benzene-1,3-dicarboxylate	78
dipropyl benzene-1,4-dicarboxylate	90

[a] Numbers in parentheses represent the ratio obtained of the two possible isomers (see text). ND = ratio of isomers was not determined. [b] Data from ref 10.

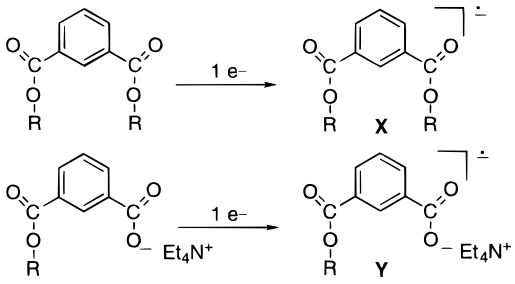
of dipropyl pyridine-2,6-dicarboxylate.[10] The yields were calculated from the weight of product obtained after methylation, extraction, and purification (see the Experimental Section). Table 2 lists the yields of the products obtained after methylation of the electrolysis solution at the completion of the bulk reductions with methyl iodide (the relative ease of methylation of the quaternary ammonium carboxylates is most likely due to the presence of the supporting electrolyte enhancing the alkylation[11]). Of course, the true electrochemical yields will be even higher.

In most cases, the ^{1}H NMR spectra for the electrolyte/product mixture recorded at the completion of the electrolysis were clean in the aromatic region, which suggested that only one product was formed. For the dicarboxylates the reaction occurred in two steps; the first step was the loss of one alkyl radical to form the monoanionic dicarboxylate, and the second step was when a more negative potential was applied (E_2 in Scheme 2), the monoanionic species reacted to form the dianionic dicarboxylate. The alkyl radicals that are proposed byproducts of the reduction were not detected voltammetrically, most likely because they quickly reacted to form hydrocarbons (either RH or RR) that were subsequently lost during the workup due to their volatility. In all cases the monoanionic product was harder to reduce than the starting material by 200−300 mV; thus, E_2 was 200−300 mV more negative than E_1. The stability of the anion radical formed by the first one-electron reduction did not influence the formation of the final product. For example, dipropyl benzene-1,4-dicarboxylate has a much more stable anion radical than dipropyl benzene-1,3-dicarboxylate, as shown by voltammetry and EPR spectroscopy,[1] although ultimately it decomposed in the same fashion to form the anionic dicarboxylate.

The reduction of the dialkyl benzene-1,3-dicarboxylates was an exception to all the other dicarboxylates in that the monoanionic dicarboxylate anion radical of this species was more stable than the parent radical. This is shown diagrammatically in Scheme 3 where species **Y** is

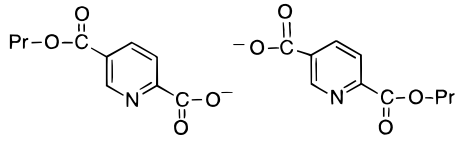
(11) Awata, T.; Baizer, M. M.; Nonaka, T.; Fuchigami, T. *Chem. Lett.* **1985**, 371.

Scheme 3



more stable than species **X**. For the equivalent species of all of the other (O) esters, **X** was more stable than **Y**. The relative stabilities of **X** and **Y** were determined by CV and EPR experiments.[1]

For the asymmetric dicarboxylates, a mixture of the two possible anionic dicarboxylates usually were obtained after the one-electron reduction. For example, the one-electron reduction of dipropyl pyridine-2,5-dicarboxylate formed the compounds shown below in approximately equal yield. The difference between the OCH_3 peaks in



the ^{1}H NMR spectrum (after the carboxylate anions had undergone methylation with MeI) was sufficiently great to confirm the existence of both isomers as products. Examination of the relative intensities of the CH_3 peaks in the ^{1}H NMR spectrum indicated that, for some of the other asymmetric dicarboxylates, one isomer was favored over the other. Integrating the peaks in the ^{1}H NMR spectra enabled the relative yields to be determined (the isomers were not separated; thus, which isomer corresponds to which relative amount is not known). For dipropyl pyridine-2,4-dicarboxylate only one isomer was obtained. For dipropyl pyridine-3,4-dicarboxylate the methyl and other alkyl peaks were not sufficiently separated in the ^{1}H NMR spectra to determine the relative yields. The ratios formed of the possible isomers are given in parentheses in Table 2.

For three compounds, dipropyl pyridine-2,5-dicarboxylate, dipropyl pyridine-2,6-dicarboxylate, and dipropyl benzene-1,3-dicarboxylate, the products of the two-electron reduction [two separate one-electron steps (E_1 and E_2) as shown in Scheme 2] were isolated and the yields calculated. The net two-electron reduction of these compounds followed by methylation of the electrolysis solution formed the dimethyl esters (85, 90, and 76% for the 2,5- and 2,6-disubstituted pyridine esters and the 1,3-disubstituted benzene ester, respectively). For the other compounds the two-electron reduction reaction was performed qualitatively in the sense that the absolute yields of products were not calculated. Methylation of the electrolysis solution at the bulk two-electron reduction stage produced compounds with nearly identical voltammetry to the starting material, indicating that the dimethylated dicarboxylates were also being formed. Analyzing the concentration by CV peak currents confirmed that the dimethylated species were being formed from the dicarboxylate dianions in high yield.

The exhaustive reduction of propyl benzoate occurred with the transfer of 1.5 ± 0.2 electrons and led to many products. After methylation and solvent extraction, examination of the reaction mixture by ^{1}H NMR spectroscopy showed that a complicated mixture of products had been formed. Methyl benzoate was evident in *ca.* 5% yield, indicating that at least a small amount of the carboxylate anion was formed. Also obtained was a small amount (*ca.* 10%) of a species with similar, but not identical, NMR to benzoylacetonitrile. The total yield of products with peaks in the aromatic region (NMR) obtained for any one experiment was less than 40% of the weight of the starting material. Examination of the residual electrolyte remaining after the organic material had been extracted showed no aromatic peaks in the ^{1}H NMR spectrum, indicating that the extraction was successful. Therefore, it is likely that a large amount of a volatile material was formed, which was subsequently lost during the workup. One possibility is the formation of benzene via complete decarboxylation. These results are in good agreement with the findings of Wagenknecht *et al.*,[2] who also reported obtaining a complicated mixture of products during the reduction of benzoate esters in acetonitrile. However, our findings differ from those of Gul'tyai *et al.*,[3] who reported obtaining the benzoate anion in quantitative yield (in DMF), and from Kistenbrugger *et al.*,[4] who reported obtaining benzoylacetonitrile in high yield (in MeCN) (we detected none). Wagenknecht *et al.* reported that the carboxylate anion was formed in higher yield at low concentrations (1 mM). We agree with this observation but suggest that the reason is due to the anion radical of the benzoate reacting with water that is present at relatively high concentrations when low concentrations of compound are electrolyzed. The addition of water to the electrolysis solution prior to the electrolysis was found to favor the formation of the carboxylate anion. The reason why the final products obtained from the reduction of the benzoate ester are different from nearly all the other esters is not clear. One possible reason is that propyl benzoate is reduced at a more negative potential than any of the other esters, close to the solvent limit, and so could undergo reactions with the solvent breakdown products formed during reduction. This could also explain why some workers[4] obtained benzoylacetonitrile as a major product. If the applied potential during the reduction is 200−300 mV more negative than the E^0 of the benzoate ester, acetonitrile and/or the electrolyte cation also will be reduced.

The reduction of dipropyl pyridine-3,5-dicarboxylate formed the dicarboxylate anion in *ca.* 30% yield plus a very complicated mixture of other products that were not identified. From the experimental data we have it is difficult to formulate a reason why this compound also differs in the products of reduction from the other esters. However, it can be noted that it does have a particularly unstable radical anion compared to the other esters.[1]

2. (S) Esters. The reduction of the (S) esters was more complicated than for the corresponding (O) esters. In contrast to the (O) esters, the stability of the radical anions formed by the one-electron reduction of the (S) esters was critical in determining the final products of CPE experiments. Two overall mechanisms have been identified as operating, which will be discussed in relation to (i) the "unstable" radical anions *S*,*S*-dipropyl pyridine-2,6-dicarbothioate (**1a**) and *S*,*S*-dipropyl benzene-1,3-dicarbothioate (**2a**), and (ii) the "stable" radical anions, *S*,*S*-dipropyl pyridine-2,5-dicarbothioate (**3a**) and *S*,*S*-dipropyl benzene-1,4-dicarbothioate (**4a**). CPC experi-

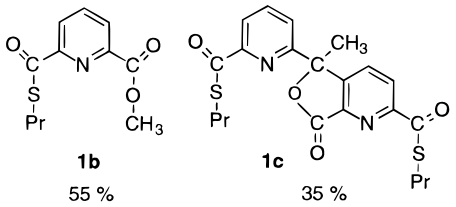
ments indicated that, similar to the (O) esters, approximately one electron was transferred per molecule. Table 1 summarizes these results at high and low concentrations.

2.1. Unstable Anion Radicals. The stability of the anion radicals formed by one-electron reduction was calculated by cyclic voltammetry and using the method of Nicholson and Shain[12] for a reversible charge transfer followed by a first-order irreversible chemical step.

$$A + e^- \leftrightharpoons A^{\bullet -}$$
$$A^{\bullet -} \xrightarrow{k_f} B$$

The ratio of i_p^{ox}/i_p^{red} (i_p^{ox} and i_p^{red} are the oxidative and reductive peak currents, respectively) was measured at a variety of scan rates and the k_f calculated at each scan rate using a working curve of i_p^{ox}/i_p^{red} *vs* $k_f\tau$ (ref 12) (τ is the time in seconds to scan from the switching potential to the $E_{1/2}$). The slope of plots of $k_f\tau$ *vs* τ yielded k_f, assuming first-order kinetics. Using this method it was found the radical anion of **2a** has a k_f of 15.7 s^{-1} and a half-life of *ca.* 40 ms. (We reported previously that the radical anion of **1a** has a k_f of 8.4 s^{-1} and a half-life of *ca.* 80 ms.)[10]

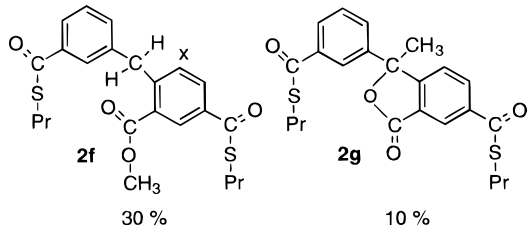
It was previously reported that the bulk reduction of **1a** formed two principal products that were isolated after methylation in high yields: methyl 6-[(propylsulfanyl)-carbonyl]pyridine-2-carboxylate (**1b**) and *S*-propyl 5-methyl-7-oxo-5-[6-[(propylsulfanyl)carbonyl]pyridin-2-yl]-5,7-dihydrofuro[3,4-*b*]pyridine-2-carbothioate (**1c**).[10]



The mechanism for the formation of **1c** was postulated to involve cleavage of the carbonyl sulfur bond in **1a** to form an acyl radical and thiolate anion, followed by aromatic substitution reactions of the acyl radical and rearrangement of the carbonyl groups to form a γ-lactone.

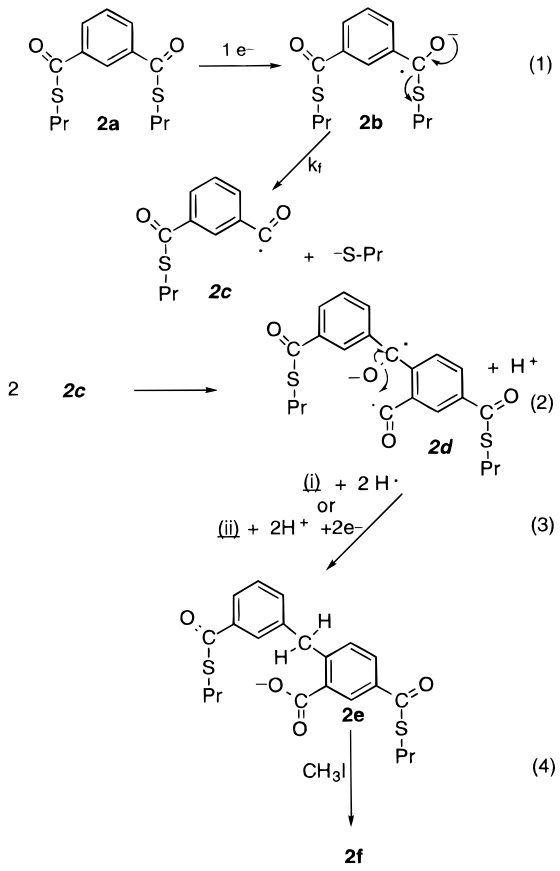
The range of products obtained from the reduction of the benzene (S) ester (**2a**) were even more extensive than those of the pyridine (S) ester (**1a**), with three compounds accounting for *ca.* 85−90% of the total yield (estimated by ^{1}H NMR spectroscopy). Two of the products are shown in Scheme 4.

Scheme 4



Compound **2g** is the benzene equivalent of **1c**, and the mechanism for its formation can be considered to be the same (refer to ref 10). The purification of these compounds was difficult due to their very similar R_f values (as determined by TLC). Compound **2g** was not able to be isolated in 100% pure form. However, the very similar nature of its NMR and IR data compared to compound **1c** provide strong evidence for the assigned structure. (The ^{1}H and ^{13}C NMR spectra of compounds **1c**, **2f**, and **2g** are provided as Supporting Information.) Importantly, the ^{13}C NMR spectrum showed a peak at 87 ppm for a quaternary carbon (confirmed by DEPT ^{13}C NMR) that is very close to the chemical shift of a carbon atom bonded to two aromatic groups, an oxygen atom and a methyl group[13] (calculated to be 85 ppm). The IR spectrum showed a carbonyl stretch at a short wavelength, which is characteristic of a γ-lactone[14] [1778 cm^{-1}, *cf.* <1740 cm^{-1} for a noncyclized (O) ester]. Compound **2f** was distinguished from another possible isomer [where the CH_2 linkage is in position **x** (Scheme 4)] by the ^{1}H NMR spectrum in the aromatic region. A sharp doublet at 7.49 ppm with a large coupling of 8.1 Hz could only be due to a proton in position **x** (Scheme 4). This proton only displays coupling to the proton adjacent to it (ortho) (coupling to protons in the para position in substituted benzenes is very small and not usually detected).[15]

Scheme 5



A plausible mechanism for the formation of **2f** is given in Scheme 5. The reaction can be considered to occur initially in a similar fashion to the reduction of **1a**; a one-electron reduction of the starting material to from a radical anion that rapidly decomposes via loss of a thiolate ion [Scheme 5 (eq 1)]. The neutral aromatic radical, ***2c***, then attacks another radical (***2c***) in the ortho position to a carbonyl group [Scheme 5 (eq 2)]. The

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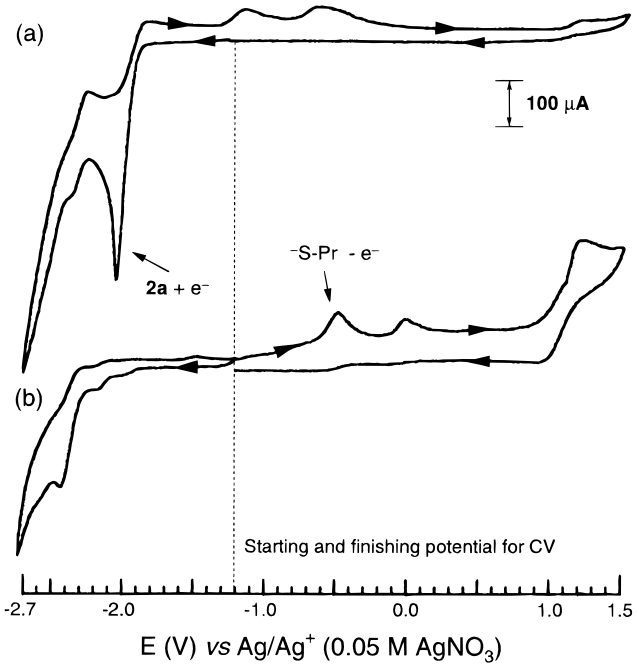


Figure 1. Cyclic voltammograms obtained at a GC electrode in MeCN (0.1 M Et_4NPF_6) using a scan rate of 100 mV s^{-1} for a 5 mM solution of *S*,*S*-dipropyl benzene-1,3-dicarbothioate (a) prior to electrolysis and (b) after the exhaustive electrolysis (1 electron per molecule) in a contolled potential electrolysis cell.

addition of (i) $2H^{\bullet}$ or (ii) $2H^+ + 2e^-$ [Scheme 5 (eq 3)] could result in species **2e**.

For (i), $H^{\bullet}$ abstraction from the solvent or the supporting electrolyte is possible. This mechanism implies that the radical has electrophilic character in order to cause the expulsion of a proton from the aromatic ring. Another possibility that cannot be discounted is in Scheme 5 (eq 2), if $H^{\bullet}$ rather than H^+ is expelled from the aromatic ring. This would require that an intermediate ketone linkage is formed between the two aromatic groups that undergoes further reduction. If this is the case, then additional electrons must be added (three to four electrons overall) to account for the formation of **2f** from **2a**. A mechanism involving the addition of two protons and $2e^-$ is less likely in an aprotic solvent [i.e., Scheme 5 (eq 3) (ii)] unless H^+ is obtained from a source other than the solvent. The total number of electrons transferred during the exhaustive electrolysis of **2a** was close to one (*ca.* 1.1), which also suggests that any intermediate species formed are not undergoing further reduction.

In support of the proposal that thiolate ions are formed during the electrochemical reduction, an oxidative peak was observed in voltammetry experiments at *ca.* −0.5 V [*vs* Ag/Ag^+ (0.05 M $AgNO_3$)]. This peak was observed (prior to the electrolysis of **2a**) on the reverse or oxidative scan of the CV only if the scan was applied in the negative potential direction first (Figure 1a). This process is due to the oxidation of any products formed at the electrode surface via the reduction of the compound. After bulk electrolysis has commenced the product(s) are present in the bulk solution and their electrochemistry now can be observed directly by linear sweep voltammetry and scanning only in the positive potential direction (Figure 1b). The oxidation potential and cyclic voltammetry of this species are very similar to that reported for thiolate ions.[16] Identical oxidation peaks were also evident after

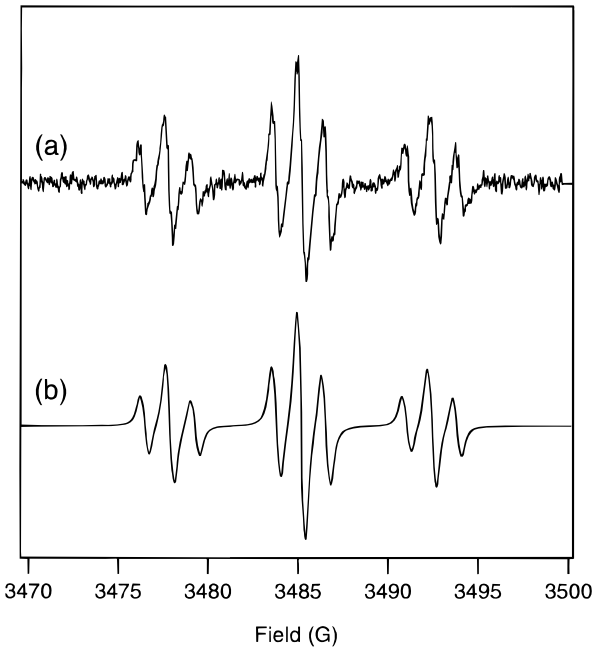


Figure 2. (a) *In situ* first-derivative EPR spectrum obtained during reductive electrolysis at a platinum electrode of a 5 mM solution of *S*,*S*-dipropyl benzene-1,3-dicarbothioate at 20 (±1) °C in MeCN (0.1 M Et_4NBF_4) in an electrochemical-EPR cell. The modulation amplitude = 0.2 G and modulation frequency = 50 kH. (b) Simulated first derivative EPR spectrum with hyperfine splitting constants for two protons of 7.3 G, two protons of 1.4 G, and two protons of 0.25 G. Simulations were calculated with a 100% Lorentzian line shape with a peak to peak line width of 0.5 G.

the commencement of reduction of **1a**. The peak(s) at *ca.* +1.2 V in Figure 1b are most likely due to either the oxidation of PrSH, formed from PrS^- reacting with trace water, or from PrS^-, reacting with aromatic protons released during the reactions of ***2c*** [see Scheme 5 (eq 2)].

EPR studies carried out during the reduction of compound **2a** lead to the detection of a radical whose spectrum is shown in Figure 2a. The rate constant for the decay of the radical in acetonitrile at 20 ± 1 °C was calculated by electrochemically generating the radical, halting the electrolysis, and measuring at constant field the signal intensity by time sweep EPR experiments (Figure 3a). The slope of a plot of ln (C_x/C_0) *vs* *t* (C_0 = signal intensity at $t = 0$ and C_x = signal intensity at varying *t*) yielded a k_f value of 0.07 s^{-1} and a $t_{1/2}$ of 10 s, assuming first-order kinetics. The first-order kinetic plot is provided in Figure 3b. The value of k_f obtained is approximately 120 times less than what was obtained voltammetrically by scan rate studies for the rate constant of compound **2b** (Scheme 5) reacting to form other compounds (*cf.* 8.4 s^{-1}). This discrepancy is considerably greater than the uncertainty in the value of k_f of the EPR-detected radical decomposing and suggests that the radical detected and monitored by EPR spectroscopy cannot be compound **2b**, but rather it must result from another intermediate species. A simulated spectrum could be fitted to the experimental data by assuming two protons have hyperfine splitting constants of *ca.* 7.3 G, two of *ca.* 1.4 G, and two of *ca.* 0.25 G (Figure 2b) that are of a reasonable magnitude for pyridine or benzene

(16) (a) Magno, F.; Bontempelli, G.; Pilloni, G. *J. Electroanal. Chem.* **1971**, *30*, 375. (b) Howie, J. K.; Houts, J. J.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 6323.

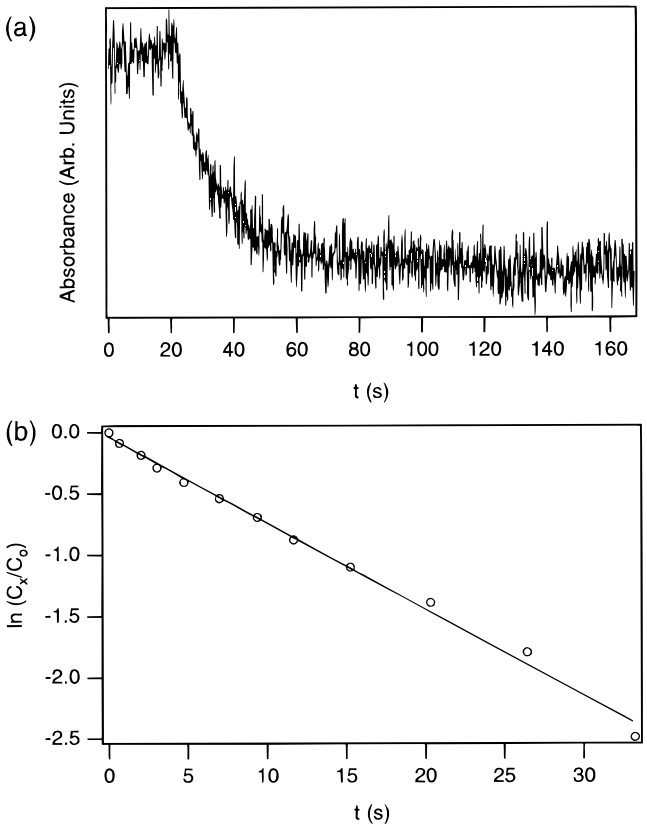
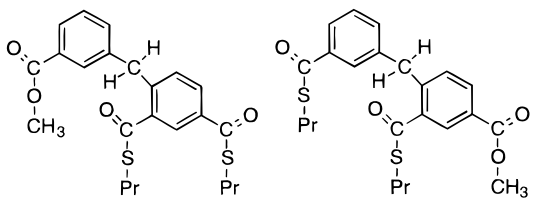


Figure 3. (a) Time sweep EPR experiment obtained by open-circuiting the potentiostat during the reductive electrolysis of a 5 mM solution of *S*,*S*-dipropyl benzene-1,3-dicarbothioate in MeCN at 20 (±1) °C (0.1 M Et_4NBF_4). Modulation amplitude = 10 G. Ordinate scale in arbitrary units. (b) Plot of ln (C_x/C_0) (C_0 = signal intensity at time $t = 0$ and C_x = signal intensity at time t) vs t (s) measured by a time sweep EPR experiment during the decay of a radical obtained by the reductive electrolysis of *S*,*S*-dipropyl benzene-1,3-dicarbothioate in MeCN at 20 (±1) °C (0.1 M Et_4NBF_4). Y intercept = −0.036, slope = −0.07, correlation coefficient (R^2) = 0.99.

esters.[1,10,17] The low number of hyperfine lines present in the EPR spectrum in Figure 2 suggests that the radical has a simple structure, and although it is not possible to positively identify the compound, complicated radicals such as dimers can be discounted. It is possible that the spectrum could arise from the acyl radical ***2c*** in Scheme 5, although this would require that two sets of non-equivalent aromatic protons have very similar coupling constants. This is analogous to the neutral radical proposed to exist during the reduction of **1a**.[10]

The NMR experiments used to identify compound **2f** do not allow the distinction between the other possible isomers shown below.

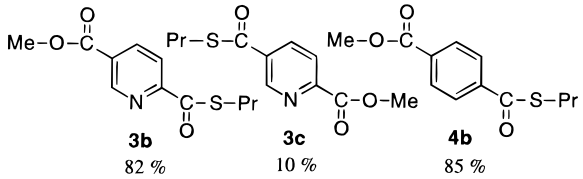


(17) (a) Gerson, F. *High Resolution E.S.R. Spectroscopy*; Wiley: New York, 1967. (b) Hirayama, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1822. (c) Hirayama, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2234. (d) Hirayama, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2530. (e) Hirayama, M.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1502.

However, the complexity of a mechanism necessary to form these isomers, particularly to account for the CH_2 linkage, greatly diminishes the probability of these being products.

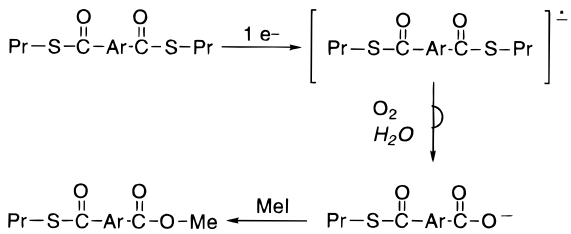
A third molecule(s) was obtained from this reaction in high yield (>20%) that has not been identified. The ^1H and ^{13}C NMR spectra of this compound are very complicated, which leads to the conclusion that the compound is either one very large molecule, containing at least four aromatic rings, or a mixture of two or more compounds with very similar polarity. Only one spot was obtained for this compound using TLC and a variety of different solvents as the eluent. Mass spectrometry did show one peak at high molecular weight (*m*/*z* 813). If this is the molecular ion, then it is *ca.* 2% of the parent ion, which is a typical value for the (O) and (S) esters (see the Supporting Information).

2.2. Stable Anion Radicals. In contrast to compounds **1a** and **1b** whose associated anion radicals are only stable for several milliseconds, the one-electron reduction of compounds **3a** and **4a** produced relatively long-lived anion radicals as deduced by voltammetric and EPR spectroscopic experiments.[1] The final products of the reductive electrolysis of compounds **3a** (formed **3b** and **3c**) and **4a** (formed **4b**) were also much simpler than for **1a** and **1b**.



Compounds **3b** and **3c** have quite different R_f values [using TLC and diethyl ether/petroleum spirits (bp 60−90 °C) 1:1 as the eluent] so they were also able to be separated and isolated in pure form by radial chromatography. The ^{13}C NMR spectra in the aromatic region for compounds **3b** and **3c** are sufficiently different to enable them to be identified and so the yields to be determined.

Scheme 6



For these compounds the anion radicals produced by one-electron reduction are so stable that they do not appreciably decay until the electrolysis solution is exposed to the atmosphere at the completion of the electrolysis and then undergo a reaction with O_2 (or $O_2^{\bullet-}$) or react with atmospheric H_2O (Scheme 6). All of the (O) and (S) esters described in this paper are reduced at a more negative potential than the reduction potential of O_2. Therefore, the mechanism depicted in Scheme 6 requires that the anion radical first reduces any O_2 present to $O_2^{\bullet-}$, and subsequently, $O_2^{\bullet-}$ reacts with the neutral (S) ester to form the carboxylate anion. This mechanism has been reported previously for (O) esters[18,19] and for one (S) ester.[19] At the completion of the electrolysis, the intense color (taken to be the radical)

remains until the solution is exposed to the atmosphere. The solution was left up to 1 h after the electrolysis before being methylated (with MeI), transferred to a flask, and then stirred overnight. Leaving the sample in the electrolysis cell for longer periods increases the amount of mixing into the auxiliary electrode compartment. The possibility of transferring the sample to a flask and methylating under an inert atmosphere was not investigated.

The results for compounds **3a** and **4a** indicate that the radicals are very stable and are not susceptible to aromatic substitution reactions on the time scale of the experiment (1−3 h).

Conclusions

In general, the one-electron reduction of pyridine and benzene *n*-alkyl (O) esters in MeCN (0.1−0.2 M Et_4NBF_4/PF_6) results in the radicals that are formed decomposing via a simple EC mechanism with loss of the alkyl fragments (most likely as radicals) to leave the carboxylate anions in high yield (*ca.* 70−100%). There does not appear to be a relationship between the stability of the anion radical and the long time scale products of the electrolysis. Benzoate and dinicotinate esters are the exception to this where much more complicated products are formed. In the case of the benzoate ester this could be due to the closeness of the E^0_f of the ester to the solvent breakdown potential limit and for the nicotinate ester due to its radical anion being very unstable.

In MeCN (with 0.1 M Et_4NBF_4/PF_6), thioic *S*-esters undergo two major types of reaction following their *ca.* one-electron bulk reduction, depending on the stability of their associated radical anions. For compounds where the radical anions are particularly unstable the radicals decompose most likely via initial loss of the thiolate ion to form an acyl radical. The neutral radical reacts further with other radicals or starting material via aromatic substitution reactions to form a range of final products that can be isolated as neutral molecules after methylation. The observation that both a pyridine and benzene (S) ester were found to react to form γ-lactones suggests that other aromatic (S) esters might also undergo a similar reaction. For compounds where the radical anions formed by a one-electron reduction are stable for long periods of time, the radicals ultimately decompose via reaction with molecular oxygen to form carboxylate anions.

Experimental Section

(1) Materials. The oxygen esters were prepared by standard methods,[20] either by refluxing the carboxylic acid in thionyl chloride to make the acid chloride and then in the corresponding alcohol to make the ester or by refluxing the carboxylic acid directly in alcohol with concd H_2SO_4. The thioic *S*-esters were prepared by refluxing the aromatic acid chloride in dichloromethane with the correct molar equivalent of propanethiol.[21] All solids were recrystallized from either methanol, methanol/water, or ether/petroleum spirits (bp 60−90 °C). Oils were purified by radial chromatography on silica gel with diethyl ether/petroleum spirits (bp 60−90 °C) as the eluent. The purity of the compounds was confirmed by NMR, mass spectrometry, TLC, and melting points for the solids. For electrochemical experiments, HPLC-grade acetonitrile (MeCN) was purified immediately prior to use by passing through a column of activated neutral alumina or by distillation over calcium hydride.[22] Other analytical-grade solvents were used as received, and laboratory-grade solvents were distilled prior to use. Electrochemical-grade tetraethylammonium tetrafluoroborate (Et_4NBF_4) and tetraethylammonium hexaflurophosphate (Et_4NPF_6) (Southwestern Analytical) were dried *in vacuo* prior to use.

(2) Voltammetry and Controlled Potential Electrolysis Procedures. For the synthetic experiments, at the completion of the bulk reductions, a 2 molar equiv of methyl iodide was added and the solution stirred for 30 min. The reduced solution was then transferred to a volumetric flask and stirred for a further 24 h. The acetonitrile was removed and a sample of the resulting electrolyte/product mixture taken for a yield estimate using quantitative ^{1}H NMR spectroscopy. The combined electrolyte/product mixture was dissolved in 50 mL of DMF and further diluted with 30 mL of water, and the methylated products were extracted using diethyl ether. Mixtures of products were further purified using radial chromatography on silica gel with diethyl ether/petroleum spirits (bp 60−90 °C) as the eluent. No aromatic compounds were detected in the water/DMF phase after extraction with ether, indicating that the methylation reaction was quantitative. The cells and equipment used for the voltammetric[10] and EPR[23] experiments have been described previously.

Reduction of propyl benzoate (1.50 g, 9.1 mmol) produced a very complicated mixture of products that were not identified (0.41 g, 27% of mass of starting material). Only small amounts of methyl benzoate were detected (2−5%).

Reduction of dipropyl benzene-1,2-dicarboxylate (1.85 g, 7.4 mmol) produced methyl propyl benzene-1,2-dicarboxylate (1.22 g, 74%): oil; R_f 0.44 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1732 (OC═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.4 Hz, 3H), 1.56−1.66 (m, 2H), 3.81 (s, 3H), 4.15 (t, J = 6.6 Hz, 2H), 7.38−7.43 (m, 2H), 7.56−7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.26, 21.76, 52.37, 67.10, 128.64, 128.74, 130.90, 131.90, 132.01, 167.40, 167.95.

Reduction of dipropyl benzene-1,3-dicarboxylate (2.00 g, 8.0 mmol) produced methyl propyl benzene-1,3-dicarboxylate (1.39 g, 78%): oil; R_f 0.54 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1735 (OC═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3H), 1.61−1.71 (m, 2H), 3.81 (s, 3H), 4.17 (t, J = 6.7 Hz, 2H), 7.37 (t, J = 7.7 Hz, 1H), 8.04−8.09 (m, 2H), 8.52−8.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 10.28, 21.91, 52.10, 66.67, 128.39, 130.40, 130.75, 133.46, 133.55, 165.53, 166.00. Unmethylated product was further reduced by one electron to form (after methylation) dimethyl benzene-1,3-dicarboxylate (1.18 g, 76%). Analytical and spectral data obtained were identical to an authentic sample.

Reduction of dipropyl benzene-1,4-dicarboxylate (1.50 g, 6.0 mmol) produced methyl propyl benzene-1,3-dicarboxylate (1.20 g, 90%): oil; R_f 0.58 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1725 (OC═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.4 Hz, 3H), 1.56−1.65 (m, 2H), 3.72 (s, 3H), 4.09 (t, J = 6.7 Hz, 2H), 7.86 (s, 2H), 7.88 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 10.19, 21.82, 52.00, 66.59, 129.18, 133.52, 133.99, 165.78, 165.31.

Reduction of propyl pyridine-2-carboxylate (0.105 g, 0.61 mmol) produced methyl pyridine-2-carboxylate (0.078 g, 93%). Spectroscopic data were identical to those of an authentic sample.

Reduction of propyl pyridine-3-carboxylate (0.107 g, 0.65 mmol) produced methyl pyridine-2-carboxylate (0.069 g,

(18) (a) Magno, F.; Bontempelli, G. *J. Electroanal. Chem.* **1976**, *68*, 337. (b) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393. (c) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640.

(19) San Filippo, J., Jr.; Romano, L. J.; Chern, C.-I.; Valantino, J. S. *J. Org. Chem.* **1976**, *41*, 586.

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(23) (a) Fiedler, D. A.; Koppenol, M.; Bond, A. M. *J. Electrochem. Soc.* **1995**, *142*, 862. (b) Webster, R. D.; Bond, A. M.; Coles, B. A.; Compton, R. G. *J. Electroanal. Chem.* **1996**, *404*, 303.

77%). Spectroscopic data were identical to those of an authentic sample.

Reduction of propyl pyridine-4-carboxylate (0.095 g, 0.58 mmol) produced methyl pyridine-4-carboxylate (0.073 g, 92%). Spectroscopic data were identical to those of an authentic sample.

Reduction of dipropyl pyridine-2,3-dicarboxylate (0.100 g, 0.40 mmol) produced methyl propyl pyridine-2,3-dicarboxylate (and propyl methyl pyridine-2,3-dicarboxylate) (0.080 g, 90%): oil; R_f 0.16 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1735 (OC═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89−0.94 (m, 3H), 1.66−1.76 (m, 2H), 3.83 and 3.90 (s, 3H), 4.20 and 4.28 (t, J = 6.7 Hz, 2H), 7.40 (dd, J = 4.8, 7.9 Hz, 1H), 8.10 (dd, J = 1.7, 7.9 Hz, 1H), 8.67 (dd, J = 1.6, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ10.22, 21.72, 52.73, 52.89, 67.61, 67.73, 124.62, 124.80, 125.86, 126.43, 137.54, 151.206, 151.59, 151.726, 165.54, 166.27.

Reduction of dipropyl pyridine-2,4-dicarboxylate (0.111 g, 0.44 mmol) produced methyl propyl pyridine-2,4-dicarboxylate (or propyl methyl pyridine-2,4-dicarboxylate) (0.083 g, 85%): oil; R_f 0.16 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1737 (OC═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.73−1.80 (m, 2H), 3.90 (s, 3H), 4.28 (t, J = 6.8 Hz), 7.93 (dd, J = 1.7, 5.0 Hz, 1H), 8.52 (s, 1H), 8.82 (d, J = 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.24, 21.89, 52.84, 67.63, 124.49, 125.80, 138.56, 149.23, 150.63, 164.39, 164.66.

Reduction of dipropyl pyridine-2,5-dicarboxylate (1.5 g, 6.0 mmol) produced methyl propyl pyridine-2,5-dicarboxylate (and propyl methyl pyridine-2,5-dicarboxylate) (1.25 g, 93%): oil; R_f 0.25 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1737, 1718 (OC═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90−0.98 (m, 3H), 1.71−1.81 (m, 2H), 3.90 and 3.95 (s, 3H), 4.26 and 4.31 (t, J = 6.6 Hz, 2H), 8.10−8.14 (m, 1H), 8.34−8.39 (m, 1H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.26, 21.88, 52.64, 53.08, 67.32, 67.75, 124.50, 128.33, 128.84, 138.15, 150.64, 150.68, 151.07, 164.30, 164.79. Unmethylated product was further reduced at −2.35 V (vs Ag/Ag^+) to form (after methylation) dimethyl pyridine-2,5-dicarboxylate (1.00 g, 85%). Analytical and spectral data obtained were identical to those of an authentic sample.

Reduction of dipropyl pyridine-3,4-dicarboxylate (0.105 g, 0.42 mmol) produced methyl propyl pyridine-3,4-dicarboxylate (and propyl methyl pyridine-3,4-dicarboxylate) (0.082 g, 88%): oil; R_f 0.22 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1740 (OC═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89−0.95 (m, 3H), 1.65−1.73 (m, 2H), 3.86 (s, 3H), 4.20−4.24 (m, 2H) 7.40−7.44 (m, 1H), 8.74 (d, J = 4.8 Hz, 1H), 8.97 and 9.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ_C 10.25, 21.77, 52.73, 52.93, 67.56, 67.85, 121.67, 121.76, 125.17, 140.24, 140.42, 150.26, 150.39, 152.67, 165.04, 165.56, 166.16, 166.67.

Reduction of dipropyl pyridine-3,5-dicarboxylate (0.103 g, 0.41 mmol) produced methyl propyl pyridine-3,5-dicarboxylate (0.027 g, 30%): mp 41−43 °C [petroleum spirits (60−90 °C)]; R_f 0.30 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1729 (OC═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3H), 1.80 (m, 2H), 3.91 (s, 3H), 4.27 (t, J = 6.7 Hz, 2H), 8.77 (t, J = 2.0 Hz, 1H), 9.34 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 10.31, 21.89, 52.55, 67.23, 125.85, 126.2, 137.81, 153.95, 154.05, 164.32, 164.81.

Reduction of *S,S*-dipropyl benzene-1,3-dicarbothioate (1.50 g, 5.3 mmol) produced **2f** (0.68 g, 30%), **2g** [0.23 g, 10% (not pure)], and one compound in high yield (*ca*. 20% weight of starting material) that was not identified. The compounds were isolated as oils. These compounds account for a high percentage of the total aromatic products of this reaction (70−90% as estimated by NMR). The low yields are, in part, a reflection of the difficulties in purification due to the very similar R_f values. TLC and NMR experiments indicated there were two other products present with peaks in the aromatic region in low yield (*ca*. 5% each).

2f: oil; R_f 0.66 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1662 (OC═O), 1726 (SC═O) cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 0.85−0.94 (m, 6H), 1.51−1.66 (m, 4H), 2.91−3.05 (m, 4H), 3.81 (s, 3H), 4.43 (s, 2H) 7.36−7.42 (m, 2H), 7.49 (d, J = 8.1 Hz, 1H), 7.70−7.73 (m, 2H), 8.00 (dd, J = 1.97, 8.0 Hz, 1H), 8.32 (d, J = 1.96 Hz, 1H); ^{13}C NMR [$(CD_3)_2SO$] δ 13.18, 22.49, 22.55, 30.36, 30.51, 38.38, 52.50, 124.89, 126.82, 128.81, 129.24, 130.21, 130.43, 132.63, 134.15, 135.05, 136.87, 141.15, 146.72, 166.53, 190.17, 191.17; EIMS m/z 430 (M^+, 2), 355 (100), 322, 165, 140, 47, 430 calcd for $C_{23}H_{26}O_4S_2$.

2g: oil; R_f 0.50 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1661 (OC═O), 1778 (SC═O); EIMS m/z 428 (M^+, 1), 353 (100), 35, 249, 146, 76, 47, 428 calcd for $C_{23}H_{24}O_4S_2$. Although this compound was not isolated in pure form, the close similarity in the NMR and IR data to compound **1c** strongly support the structure assigned (see the Supporting Information for spectra).

Reduction of *S,S*-dipropyl pyridine-2,5-dicarbothioate (0.124 g, 0.44 mmol) produced methyl-2-[(propylthio)carbonyl]-pyridine-5-carboxylate (**3b**) (0.086 g, 82%) and methyl 5-[(propylthio)carbonyl]pyridine-2-carboxylate (**3c**) (0.011 g, 10%).

3b: mp 46−47 °C (ether); R_f 0.55 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1666 (OC═O), 1724 (SC═O); ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.3 Hz, 3H), 1.65−1.73 (m, 2H), 3.07 (t, J = 7.2 Hz, 2H), 3.99 (s, 3H), 8.17 (d, J 8.1 Hz, 1H), 8.31 (dd, J = 2.2, 8.2 Hz, 1H), 9.20 (d, J 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.32, 22.66, 31.21, 53.17, 124.87, 134.85, 135.60, 148.23, 150.79, 164.74, 189.58; EIMS m/z 239 (M^+, 1), 211, 164, 136 (100), 92, 77, 59, 239 calcd for $C_{11}H_{13}NO_3S$.

3c: mp 42−44 °C (ether); R_f 0.30 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1661 (OC═O), 1721 (SC═O); ^1H NMR ($CDCl_3$) δ 1.01 (t, J = 7.4 Hz, 3H), 1.65−1.72 (m, 2H), 3.01 (t, J = 7.1 Hz, 2H), 3.95 (s, 3H), 7.99 (dd, J = 0.7, 7.7 Hz, 1H), 8.40 (dd, J = 2.1, 8.2 Hz, 1H), 9.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.45, 22.57, 30.76, 52.71, 119.77, 129.13, 138.44, 150.16, 154.45, 164.79, 189.54, 192.88; EIMS m/z 239 (M^+, 1), 164 (100), 136, 106, 78, 59, 239 calcd for $C_{11}H_{13}NO_3S$.

Reduction of *S,S*-dipropyl benzene-1,4-dicarbothioate (0.114 g, 0.40 mmol) produced methyl-4-[(propylthio)carbonyl]-pyridine-1-carboxylate (**4b**) (0.081 g, 85%): oil; R_f 0.59 [ether/petroleum spirits (60−90 °C) 1:1]; IR (KBr) 1665 (OC═O), 1729 (SC═O); ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 3H), 1.68 (m, 2H), 3.04 (t, J = 7.1 Hz, 4H), 3.90 (s, 3H) 7.97 (dd, J = 1.9, 6.9 Hz, 2H), 8.06 (dd, J = 1.59, 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.35, 22.78, 31.088, 52.37, 127.02, 129.73, 133.93, 140.46, 166.06, 191.47.

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Supporting Information Available: ^1H and ^{13}C NMR (including in some cases INEPT or DEPT) spectra of all new products of the reductions and spectral data of starting esters (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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